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Optically Active Imidazole *N*-Oxides Derived from L-Prolinamine[‡]

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ABSTRACT

Starting with (*S*)-1-benzylprolinamine and α-hydroxyimino ketones, enantiomerically pure bisheterocyclic imidazole *N*-oxides bearing the (*S*)-configured *N*-benzyl(pyrrolidin-2-yl)methyl residue were prepared. These *N*-oxides reacted with 2,2,4,4-tetramethylcyclobutane-1,3-dithione to give the corresponding optically active imidazole-2-thione derivatives via sulfur transfer reaction. Reduction of the *N*-oxides with Raney-nickel led to deoxygenation, whereas catalytic hydrogenation (Pd/C) in ethanol occurred with simultaneous deoxygenation and debenzylation, leading to optically active 1-(pyrrolidin-2-ylmethyl)-1*H*-imidazoles. Alkylation of the prepared imidazole *N*-oxides and the respective imidazoles with butyl and hexylbromide and subsequent anion exchange gave optically active *N*-alkoxy- and *N*-alkylimidazolium tetrafluoroborates, respectively, with the properties of 'room temperature ionic liquids'.

1. Introduction

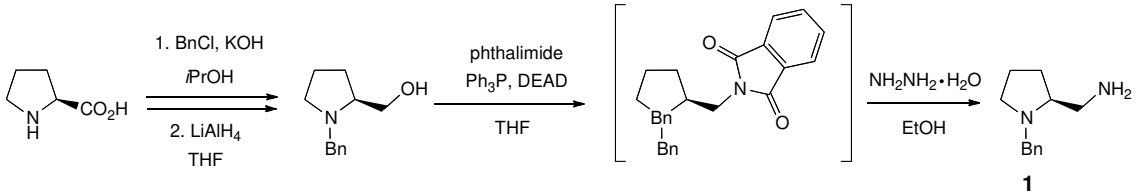
The importance of imidazole derivatives in organic, bioorganic, and medicinal chemistry as well as in materials science is well documented.[2-4] In recent years, numerous reports on the synthesis and diverse applications of imidazole *N*-oxides were published.[5] In contrast to six-membered N-heterocycles, imidazoles cannot be converted to the corresponding N-oxides by treatment with typical oxidizing reagents.[6] Therefore, condensations of ♋-hydroxyimino ketones with methylidene amines (formaldehyde imines) were applied as a convenient access to 2-unsubstituted imidazole *N*-oxides.[5a,7] Starting with optically active primary amines, such as 1-phenylethylamine, *trans*-cyclohexane-1,2-diamine, as well as ♋-amino acid esters, the desired enantiomerically pure imidazole N-oxides were obtained as sole products.[8] Some of them were tested as ligands for asymmetric allylation of aldehydes[9] and in cyclopropanation reactions.[10]

L-Prolinamine ((2*S*)-pyrrolidin-2-yl)methylamine) is a very useful and widely applied building block for the synthesis of optically active ligands of potential importance for asymmetric synthesis.[11] The non-protected prolinamine easily reacts with electron-deficient dicyanofumarates, and enantiomerically pure bicyclic pyrazinones were obtained chemoselectively.[12]

The aim of the present study was the synthesis of new series of optically active imidazole derivatives containing the chiral pyrrolidine fragment originating from L-prolinamine. Some of the products were used for the preparation of new imidazole-based optically active ionic liquids.

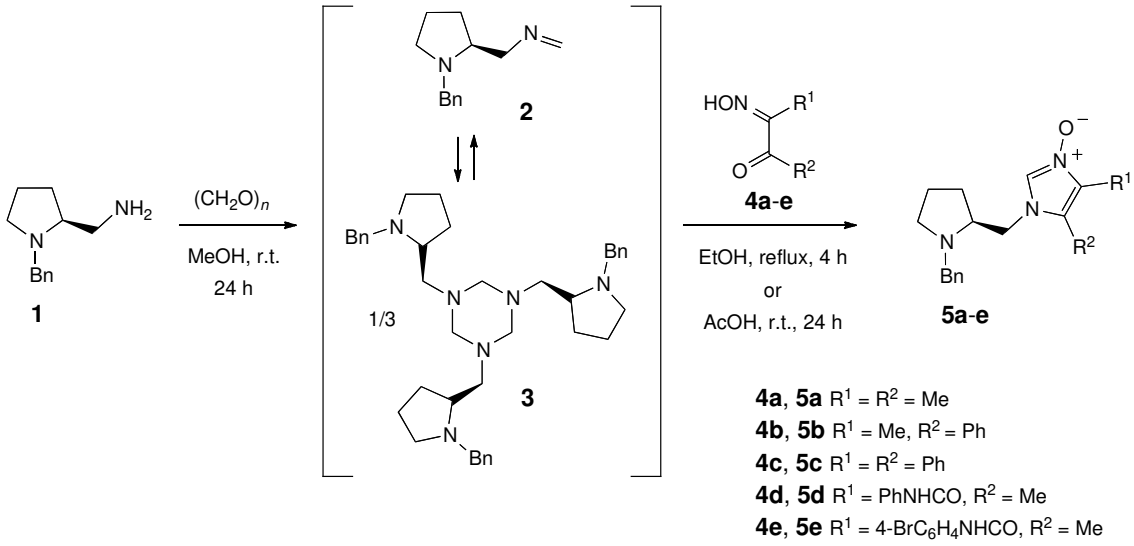
2. Results and discussion

The preparation of the starting *N*-benzylated L-prolinamine (**1**) can be achieved from methyl L-prolinate *via* aminolysis and reduction of the amide[13] or from L-prolinol *via* the intermediate azide.[11a] In addition, we developed a new approach to **1b** based on a Mitsunobu reaction *via* the intermediate phthalimide derivative (Scheme 1).



Scheme 1.

The condensation of **1** with paraformaldehyde led to methylidene prolinamine **2**, which spontaneously underwent trimerization to give the corresponding hexahydrotriazine **3** (Scheme 2). The structure of **3** was confirmed by the ^{13}C-NMR spectrum, in which no signal for the imino group (N=CH_2) appears. The trimerization of methylidene amines is a typical reaction,[14] and only in the case of bulky substituents, *e.g*. adamantan-1-yl, the monomeric form is stable under standard conditions.[15] In the case of the present study, the trimer **3** is believed to exist in solution in an equilibrium with the monomeric form **2**.



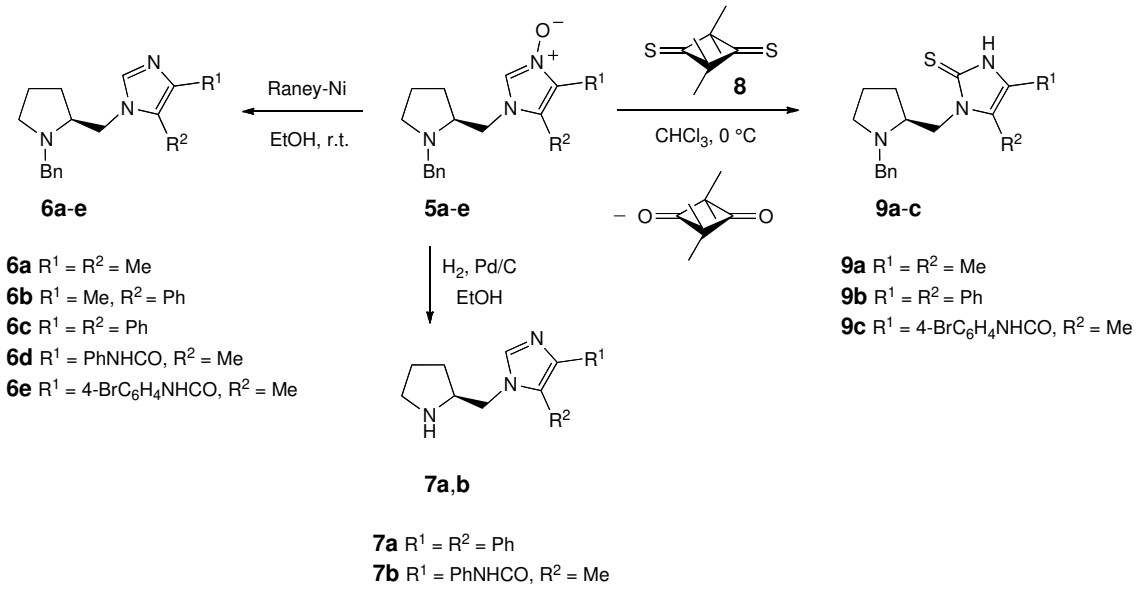
Scheme 2.

The latter reacts with ♋-hydroxyimino ketones **4a**-**e** in boiling ethanol (method A) or in glacial acetic acid at room temperature (method B) yielding the desired optically active imidazole *N*-oxides **5a**-**e** in good yields (Scheme 2). In order to examine the enantiopurity of these products, a sample of **5a** was dissolved in $CDCl_3$ with an equimolar amount of (*tert*-butyl)(phenyl)thiophosphinic acid (MOD reagent).[16] The ^{1}H-NMR spectrum showed only one set of signals, whereas in the case of racemic **5a** (*rac*-**5a**), addition of MOD led to the appearance of two sets. Thus, in the racemic product, the diagnostic H-C(2) signal of imidazole *N*-oxides appeared as two singlets located at 8.87 and 8.86 ppm. Similarly, one Me group gave two singlets at 1.95 and 1.94 ppm, whereas the second Me group of both enantiomers absorbed as a singlet at 2.08 ppm. Moreover, for all other signals observed, duplication was observed in the spectrum of *rac*-**5a**.

Based on this result, we assumed that all prepared imidazole *N*-oxides **5** are enantiomerically pure. The same conclusion was formulated in the case of other optically active imidazole *N*-oxides described in our previous papers.[8]

2-Unsubstituted imidazole *N*-oxides are versatile starting materials for the preparation of other imidazole derivatives, such as the parent imidazoles,[8] imidazole-2-thiones,[8] imidazolones,[17] and (imidazol-2-yl)acetates.[18] In addition, imidazole *N*-oxides or the corresponding parent compounds have been alkylated to give imidazolium salts, which display properties of ionic liquids.[8d,19]

Treatment of imidazole *N*-oxides **5** with Raney-Ni in ethanol at room temperature led smoothly to selective deoxygenation to yield the corresponding imidazoles **6** (Scheme 3). Under these conditions, no debenzylation of the pyrrolidine ring was observed. In a control experiment, the reaction mixture was heated to reflux, and in this case, a complex mixture of products was formed. On the other hand, hydrogenolysis (H_2, Pd/C) of **5c** and **5d** in ethanol led to deoxygenation and debenzylation to yield **7a** and **7b**, respectively.

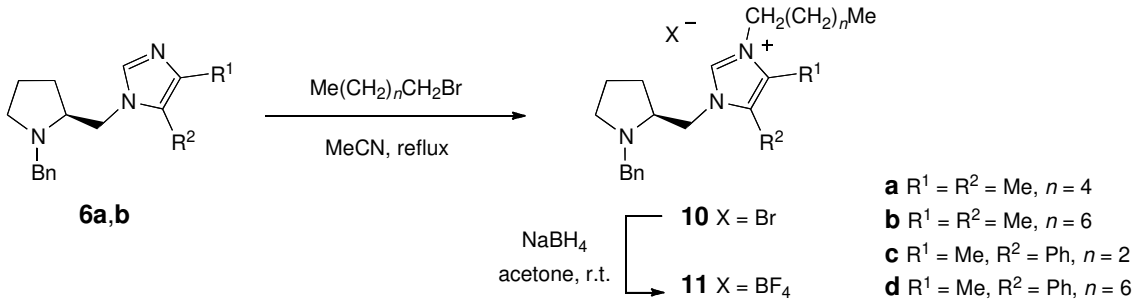


Scheme 3

The 2-unsubstituted imidazole *N*-oxides **5a**,**c** and **e** reacted with 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**8**) via the so-called 'sulfur-transfer reaction' to give optically active imidazole-2-thiones **9a-c** (Scheme 3).[20] In these reactions, imidazole *N*-oxides **5** react as 'nitrone-like' 1,3-dipoles, and after the 1,3-dipolar

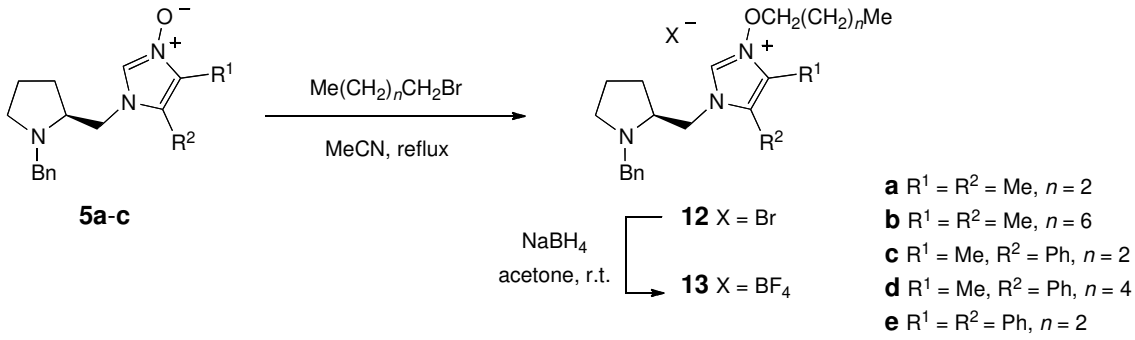
cycloaddition, the intermediate 1,4,2-oxathiazolidine undergoes a fragmentation to yield **9** and 2,2,4,4-tetramethyl-3-thioxocyclobutanone. The latter can undergo the 'sulfur-transfer reaction' with a molecule **5** once more, leading to **9** and 2,2,4,4-tetramethylcyclobutane-1,3-dione. The obtained imidazole-2-thiones **9** are characterized by the thiourea moiety, which is of great importance in asymmetric synthesis and organocatalysis.[21]

The alkylation of imidazoles with long-chain alkyl bromides and subsequent anion exchange is a typical procedure for the preparation of imidazolium salts with the characteristic behavior of ionic liquids (ILs).[22] Optically active ionic liquids are of special interest, but to date, proline-derived examples are rare.[23] Thus, imidazoles **6** were alkylated with butyl, hexyl, and octyl bromide in boiling acetonitrile. The obtained imidazolium bromides **10** dissolved in acetone were treated with an equimolar amount of $NaBF_4$ at room temperature to give the corresponding tetrafluoroborates **11** (Scheme 4). All of them are liquids at room temperature and, therefore, belong to the class of optically active 'room temperature ionic liquids' (RTILs).



Scheme 4

In a recent paper, we described the synthesis of a new type of ionic liquids containing a 3-alkoxyimidazolium cation.[8d] Similary, the alkylation of imidazole *N*-oxides **5** were carried out with equimolar amounts of the respective alkyl bromides in $CHCl_3$ solution at room temperature to give imidazolium bromides **12** (Scheme 5). The latter were transformed to the corresponding tetrafluoroborates **13** in the usual way. It is worth mentioning that under the applied reaction conditions the alkylation of compounds **5** and **6** occurred selectively at the imidazole fragment.



5a-c

Scheme 5

3. Conclusions

The results described in the present paper show that *N*-benzyl L-prolinamine is a useful starting material for the preparation of a new type of optically active 2-unsubstituted imidazole *N*-oxides. Based on the known reactivity of these *N*-oxides, they can be converted to a variety of other optically active imidazole derivatives such as the parent imidazoles and imidazole-2-thiones. The debenzylation with simultaneous deoxygenation of imidazole *N*-oxides **5** leading to imidazoles of type **7** can be achieved conveniently by hydrogenolysis under standard conditions. Alkylation of the prepared imidazole *N*-oxides as well as the corresponding imidazoles leads to *N*-alkoxyimidazolium and *N*-alkylimidazolium salts, respectively, with the properties of optically active 'room temperature ionic liquids' (RTILs).

The optically active products described in the present study are of interest as potential ligands for asymmetric synthesis and for organocatalysis. The easily available ionic liquids can be used as reaction media for small-scale organic synthesis.

4. Experimental

4.1. General

Melting points were determined in a capillary using a Melt-Temp. II apparatus (Aldrich) or STUART SMP30 and are uncorrected. The IR Spectra were recorded on a NEXUS FT-IR spectrophotometer in KBr; absorptions (ν) in cm^{-1}. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were measured on a Bruker Avance III instrument (600 and 150 MHz, resp.) using solvent signal as reference. Multiplicity of signals in the ^{13}C NMR spectra was established using HMQC technique. Chemical shifts (´) are given in ppm and coupling constants *J* in Hz. Assignments of signals in ^{13}C NMR spectra were made on the basis of HMQC experiments. HR-MS: Bruker maXis spectrometer; ESI-MS: Varian

500. Optical rotations were determined on a PERKIN-ELMER 241 MC polarimeter for » = 589 nm.

4.2. Starting Materials

All solvents and reagents are commercially available and used as received. (2*S*)-Benzylproline[24] and ±-hydroxyimino ketones **4**[20a] were prepared according to known procedures.

4.2.1. [(2*S*)-*N*-Benzylpyrrolidin-2-yl]methanol (*N*-benzylprolinol)

A solution of (2*S*)-benzylproline (3 g, 14.6 mmol) in THF (30 ml) was cooled to 0 °C and a suspension of $LiAlH_4$ in THF (2M, 21.9 mmol, 12.4 ml) was added dropwise. The mixture was stirred overnight at rt. Next, an aqueous solution of KOH (10%, 15 ml) was added and the organic product was extracted with Et_2O (3×15 ml). The organic layers were combined and dried (Na_2SO_4). After filtration, the solvent was evaporated and the crude, oily product was distilled in a Kugel-Rohr (75–78 °C, 0.1 hPa). Yield: 2.0 g (71%). Colorless oil. IR (film): *v* 3405br, 2961m, 2872m, 2799m, 1879w, 1810w, 1721w, 1496m, 1453m, 1211m, 1049w, 1029w, 849m, 839s, 699s. ^{1}H NMR ($CDCl_3$): ´ 7.32–7.25 (m, 5H, HC(arom.)); 3.92, 3.32 (AB, J_{AB} = 12.9, 2H, H_2C–Ph); 3.61 (dd, $^2J_{H,H}$ = 10.8, $^3J_{H,H}$ = 3.6, 1H, H_2C–OH); 3.38 (dd, $^2J_{H,H}$ = 10.8, $^3J_{H,H}$ = 1.8, 1H, H_2C–OH); 2.96–2.90 (m, 1H, $H_2C(5)$); 2.72–2.65 (m, 1H, HC(2)); 2.29–2.22 (m, 1H, $H_2C(5)$); 1.93–1.85 (m, 1H, $H_2C(3)$); 1.82–1.75 (m, 1H, $H_2C(3)$); 1.71–1.59 (m, 2H, $H_2C(4)$). ^{13}C NMR ($CDCl_3$): ´ 139.4 (1 C(arom.)); 128.7, 128.3, 127.1 (5 CH(arom.)); 64.3 (C(2)); 61.8 (CH_2–OH); 58.6 (CH_2–Ph); 54.5 (C(5)); 27.8 (C(3)); 23.5 (C(4)). $[\pm]_D^{25}$ = –58 (*c* = 1.0, $CHCl_3$); lit.[25] $[\pm]_D^{25}$ –59.9 (*c* = 1.0, $CHCl_3$).

4.2.2. 1-[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methanamine 1

To the solution of triphenylphosphine (0.86 g, 3.3 mmol) and phthalimide (0.48 g, 3.3 mmol) in THF (10 ml), *N*-benzylprolinol (0.57 g, 3.0 mmol) dissolved in THF (2 ml) was added, and the solution was stirred magnetically for 10 min. After this time, diethyl azodicarboxylate (DEAD) (0.62 g, 3.6 mmol) was added dropwise, and the mixture obtained was heated at reflux for 8 h. Next, the solvent was removed under reduced pressure, the obtained residue was suspended in Et_2O (50 ml) and stirred for 1

h. Then, the precipitate was separated by filtration and the filtrate was removed under reduced pressure. The residue was dissolved in EtOH (20 ml), subsequently hydrazine monohydrate (0.4 g, 8.0 mmol) was added, the mixture was heated at reflux for 2 h, and after addition of HCl (1M, 3 ml) heating was continued for 30 min. The precipitate was filtered off and the solvents were removed under reduced pressure. The residue obtained was treated with aqueous NaOH (1M, 5 ml), the organic product was extracted with Et_2O (3×25 ml), and the combined organic layers were dried (Na_2SO_4). After filtration, the Et_2O solution was concentrated under reduced pressure to give **1** as a pale yellow oil. The crude product was distilled in a Kugel Rohr (50–52 ^oC, 0.1 hPa). Yield: 0.4 g (70%). Colorless oil. IR (film): *v* 3365m, 3289br, 3027m, 2961m, 2871m, 2791m, 1950m, 1877m, 1810m, 1495s, 1453s, 1372m, 1121m, 1072m, 1028s, 910m, 738s, 699s. ^{1}H NMR ($CDCl_3$): ´ 7.38–7.19 (m, 5H, HC(arom.)); 3.96, 3.30 (AB, J_{AB} = 12.9, 2H, H_2C–Ph); 2.97–2.90 (m, 1H, $H_2C(5)$); 2.75 (dd, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 5.4, 1H, H_2C–NH_2); 2.70 (dd, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 3.6, 1H, H_2C–NH_2); 2.58–2.53 (m, 1H, HC(2)); 2.25–2.17 (m, 1H, $H_2C(5)$); 1.95–1.87 (m, 1H, $H_2C(3)$); 1.77–1.63 (m, 2H, $H_2C(4)$; 1H, $H_2C(3)$). ^{13}C NMR ($CDCl_3$): ´ 139.9 (1 C(arom.)); 128.7, 128.7, 126.8 (5 CH(arom.)); 65.5 (C(2)); 59.1 (CH_2–Ph); 54.6 (C(5)); 44.1 (CH_2–NH_2); 28.0 (C(3)); 23.0 (C(4)) ppm. $[\pm]_D^{25}$ = –54 (*c* = 1.0, CH_2Cl_2); lit.[26] $[\pm]_D^{25}$ = –55 (*c* = 9.97, $CHCl_3$).

4.2.3. 1-[(2*S*)-*N*-Benzylpyrrolidin-2-yl]-*N*-methylidenemethanamine 2 resp. 3

To a magnetically stirred solution of **1** (1.81 g, 9.53 mmol) in MeOH (10 ml), paraformaldehyde (0.30 g, 10 mmol) was added, and the mixture was stirred overnight at rt. Then, the solvent was removed under reduced pressure. The oil obtained was used in the next step without purification. Yield: 1.92 g (98%). Pale yellow oil. IR (film): *v* 3361br, 3085m, 3061m, 3026m, 2960m, 2872m, 2788m, 1946m, 1875m, 1808m, 1604m, 1495s, 1453s, 1604m, 1155w, 1028m, 916m, 735s, 698s. ^{1}H NMR ($CDCl_3$): ´ 7.35–7.16 (m, 5H, HC(arom.)); 4.16, 3.23 (AB, J_{AB} = 13.2, 2H, H_2C–Ph); 3.47–3.32 (br, 2H, N–CH_2–N); 2.93–2.87 (m, 1H, HC(5)); 2.68 (dd, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 4.8, 1H, H_2C–N); 2.57–2.52 (m, 1H, HC(2)); 2.42 (dd, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 6.6, 1H, H_2C–N); 2.15–2.09 (m, 1H, HC(5)); 1.98–1.88 (m, 1H, HC(3)); 1.75–1.60 (m, 2H, $H_2C(4)$; 1H, $H_2C(3)$). ^{13}C NMR ($CDCl_3$): ´ 139.9 (C(arom.)); 128.9, 128.2, 126.7 (5, CH(arom.)); 75.8 (N–CH_2–N); 62.4 (C(2)); 59.6 (CH_2–Ph); 57.6 (CH_2–N); 54.2 (C(5)); 30.2 (C(3)); 22.6 (C(4)). ESI–MS: *m/z* 203 (100, $[M+1]^+$). $[\pm]_D^{25}$ = –14 (*c* = 1.0, CH_2Cl_2).

4.2.4. Synthesis of imidazole *N*-oxides 5

Procedure A: A solution of **2** (10 mmol) and the corresponding ±-hydroxyimino ketone **4** (10 mmol) in EtOH (5 ml) was heated at reflux for 3 h. Next, the solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography or by crystallization.

Procedure B: A mixture of **2** (10 mmol) and of the corresponding **4** (10 mmol) in glacial acetic acid (15 ml) was magnetically stirred overnight at rt. Then, HCl gas was bubbled through the mixture for 1 h. Next, Et_2O (ca. 100 ml) was added and the colorless precipitated hydrochloride was filtered, washed with cold Et_2O (3×20 ml), and dried under reduced pressure. The crude hydrochloride was dissolved in CH_2Cl_2 (25 ml), solid $NaHCO_3$ (1.5 g) was added, and stirring was continued for 1 h until evolution of CO_2 ceased. The inorganic salts were filtered off and the solvent was removed. The crude products **5a**-**e** were purified by column chromatography or by crystallization.

4.2.4.1. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-4,5-dimethyl-1*H*-imidazole 3-oxide 5a

Yield: 2.5 g (88%). Colorless oil (SiO_2, MeOH/AcOEt, 1:1). IR (film): *v* 3584–3028br, 2954m, 2926m, 2807m, 1627m, 1495m, 1453s, 1381m, 1338m, 1148m, 1041s, 843w, 733w, 702s. ^{1}H NMR ($CDCl_3$): ´ 7.94 (s, 1H, HC(2)); 7.35–7.21 (m, 5H, HC(arom.)); 3.75, 3.54 (AB, J_{AB} = 12.6, 2H, H_2C–Ph); 3.68 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 4.8, 1H, H_2C–N); 3.60 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 6.0, 1H, H_2C–N); 3.04–2.99 (m, 1H, H_2C(5')); 2.92–2.86 (m, 1H, HC(2')); 2.39–2.32 (m, 1H, H_2C(5')); 2.15 (s, 3H, H_3C–C(4)); 2.05 (s, 3H, H_3C–C(5)); 1.93–1.85 (m, 1H, H_2C(3')); 1.75–1.69 (m, 1H, H_2C(4')); 1.68–1.59 (m, 1H, H_2C(4')); 1.49–1.43 (m, 1H, H_2C(3')). ^{13}C NMR ($CDCl_3$): ´ 138.9 (C(arom.)); 128.8, 128.5, 127.3 (5 CH(arom.)); 126.3 (1 C(imid.)); 124.9 (HC(2)); 121.0 (1 C(imid.)); 63.2 (HC(2')); 60.1 (CH_2–Ph); 54.8 (C(5')); 49.1 (CH_2–N); 28.5 (C(3')); 23.3 (C(4')); 8.9 (CH_3–C(4)); 7.3 (CH_3–C(5)). HR-ESI-MS (MeOH + HCOOH): 286.1909 (calcd 286.1914 for $C_{17}H_{24}N_3O$, $[M+1]^+$). $[\pm]_D^{25}$ = –18 (*c* = 1.0, CH_2Cl_2).

4.2.4.2. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-4-methyl-5-phenyl-1*H*-imidazole 3-oxide 5b

Yield: 1.3 g, 40% (method A), 2.7 g, 80% (method B). Colorless oil (SiO_2, MeOH/AcOEt, 1:1). IR (film): *v* 3647–3028br, 2962m, 2876m, 2803m, 1683s, 1551m, 1496s, 1452m, 1381m, 1028m, 922w, 847w, 764m, 734m, 702m, 642s. ^{1}H NMR ($CDCl_3$): ´ 8.29 (s, 1H, HC(2)); 7.49–7.45 (m, 3H, HC(arom.)); 7.32–7.29 (m, 2H, HC(arom.)); 7.26–7.24 (m, 3H, HC(arom.)); 7.23–7.20 (m, 2H, HC(arom.)); 3.77 (dd, $J_{H,H}$ = 14.4, $J_{H,H}$ = 4.8, 1H, H_2C–N); 3.64–3.58 (m, 1H, H_2C–Ph, 1H, H_2C–N); 3.38 (AB, J_{AB}= 12.9, 2H, H_2C–Ph); 2.96–2.91 (m, 1H, $H_2C(5')$); 2.71–2.68 (m, 1H, $H_2C(2')$); 2.28–2.22 (m, 1H, $H_2C(5')$); 2.19 (s, 3H, H_3C–C(4)); 1.75–1.73 (m, 1H, $H_2C(3')$); 1.63–1.60 (m, 1H, $H_2C(4')$); 1.53–1.48 (m, 1H, $H_2C(4')$); 1.33–1.29 (m, 1H, $H_2C(3')$). ^{13}C NMR ($CDCl_3$): ´ 138.3 (1 C(arom.)); 130.7, 129.8, 129.4, 129.1, 129.1, 128.6, 127.5, 127.2 (9 signals for 10 CH(arom.), 2 C(arom.), 1 HC(2), 2 C(imid.)); 63.4 (HC(2')); 59.7 (CH_2–Ph); 54.5 (C(5')); 49.5 (CH_2–N); 28.5 (C(3')); 23.3 (C(4')); 7.9 (H_3C–C(4)). HR-ESI-MS (MeOH + HCOOH): 348.2068 (calcd 348.2070 for $C_{22}H_{26}N_3O$, $[M+1]^+$). $[\pm]_D^{25}$ = –24 (*c* = 1.0, CH_2Cl_2).

4.2.4.3. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-4,5-diphenyl-1*H*-imidazole 3-oxide 5c

Yield: 2.6 g, 65% (method A), 3.1 g, 75% (method B). Colorless crystals. Mp 160–161 °C ($CHCl_3$/Et_2O). IR (KBr): *v* 3646–3027br, 2961m, 2876w, 2810m, 1736m, 1604m, 1495m, 1445m, 1346m, 1193m, 1076m, 1039s, 918m, 864s, 762s, 700s, 656m. ^{1}H NMR ($CDCl_3$): ´ 8.35 (s, 1H, HC(2)); 7.55–7.52 (m, 2H, HC(arom.)); 7.43–7.36 (m, 3H, HC(arom.)); 7.32–7.28 (m, 2H, HC(arom.)); 7.27–7.19 (m, 8H, HC(arom.)); 3.75 (dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 4.2, 1H, H_2C–N); 3.62 (dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 6.0, 1H, H_2C–N); 3.63, 3.39 (AB, J_{AB} = 13.2, 2H, H_2C–Ph); 2.98–2.93 (m, 1H, $H_2C(5')$); 2.79–2.72 (m, 1H, HC(2')); 2.31–2.24 (m, 1H, $H_2C(5')$); 1.84–1.76 (m, 1H, $H_2C(3')$); 1.69–1.62 (m, 1H, $H_2C(4')$); 1.60–1.51 (m, 1H, $H_2C(4')$); 1.43–1.37 (m, 1H, $H_2C(3')$). ^{13}C NMR ($CDCl_3$): ´ 138.7 (1 C(arom.)); 131.0, 130.2, 129.6, 129.5, 129.1, 128.8, 128.5, 128.1, 128.0, 127.7, 127.3, 127.3, 126.7 (2 C(arom.), 15 HC(arom.), 2 C(imid.)); 126.9 (HC(2)) 63.1 (HC(2')); 59.6 (CH_2–Ph); 54.4 (C(5')); 49.1 (CH_2–N); 28.4 (C(4')); 23.2 (C(3')). ESI HR-ESI-MS (MeOH + HCOOH): 410.2228 (calcd 410.2227 for $C_{27}H_{28}N_3O$, $[M+1]^+$). $[\pm]_D^{25}$ = –5 (*c* = 1.0, CH_2Cl_2).

4.2.4.4. *N*-Phenyl-1-{[(2*S*)-*N*-benzylpyrrolidin-2-yl]methyl}-5-methyl-1*H*-imidazole-4-carboxamide 3-oxide 5d

Yield: 3.0 g (78%). Colorless crystals. Mp 120–122 °C (Et_2O). IR (KBr): *v* 3427br, 3171m, 3062m, 2978w, 2921w, 2798m, 1672s, 1619m, 1598m, 1560s, 1310s, 1273s, 759m, 750m, 701m, 630m. ^{1}H NMR ($CDCl_3$): ´ 12.98 (s, 1H, NH); 7.95 (s, 1H, HC(2)); 7.74–7.69 (m, 2H, HC(arom.)); 7.36–7.31 (m, 4H, HC(arom.)); 7.34–7.24 (m, 4H, HC(arom.)); 3.76, 3.63 (AB, J_{AB} = 13.6, 2H, H_2C–Ph); 3.76 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 4.8, 1H, H_2C–N); 3.66 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 5.40 Hz, 1H, H_2C–N); 3.10–3.04 (m, 1H, H_2C'(5)); 3.02–2.96 (m, 1H, H_2C'(2)); 2.58 (s, 3H, H_3C–C(5)); 2.47–2.40 (m, 1H, H_2C(5')); 2.00–1.91 (m, 1H, H_2C(3')); 1.80–1.73 (m, 1H, H_2C(4')); 1.65–1.56 (m, 1H, H_2C(4')); 1.48–1.41 (m, 1H, H_2C(3')). ^{13}C NMR ($CDCl_3$): ´ 157.9 (C=O); 138.7, 138.4 (2 C(arom.)); 131.5, 129.1, 129.0, 128.8, 127.7, 124.2, 121.7, 120.1 (10 CH(arom.), 2 C(imid.)); 126.0 (HC(2)); 62.8 (HC(2')); 60.3 (CH_2–Ph); 55.0 (C(5')); 48.7 (CH_2–N); 28.4 (C(3')); 23.7 (C(4')); 10.0 (H_3C–C(5)). HR-ESI-MS (MeOH + HCOOH): 391.2124 (calcd 391.2129 for $C_{23}H_{27}N_4O_2$, $[M+1]^+$). $[\pm]_D^{25}$ = –27 (*c* = 1.0, CH_2Cl_2).

4.2.4.5. *N*-(4-Bromophenyl)-1-{[(2*S*)-*N*-benzylpyrrolidin-2-yl]methyl}-5-methyl-1*H*-imidazole-4-carboxamide 3-oxide 5e

Yield: 3.8 g (81%). Colorless crystals. Mp 168–170 °C (Acetone). IR (KBr): *v* 3432br, 3077m, 2975w, 2939w, 2919w, 2802m, 1675s, 1612s, 1556s, 1488s, 1309m, 1069m, 817m, 757m, 702s, 636m, 503m. ^{1}H NMR ($CDCl_3$): ´ 13.00 (s, 1H, NH); 7.91 (s, 1H, HC(2)); 7.63–7.59 (m, 2H, HC(arom.)); 7.45–7.41 (m, 2H, HC(arom.)); 7.35–7.31 (m, 2H, HC(arom.)); 7.29–7.25 (m, 3H, HC(arom.)); 3.65, 3.54 (AB, J_{AB} = 12.6, 2H, H_2C–Ph); 3.67 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 4.8, 1H, H_2C–N); 3.57 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 5.4, 1H, H_2C–N); 3.09–3.03 (m, 1H, H_2C(5')); 3.02–2.95 (m, 1H, H_2C(2')); 2.55 (s, 3H, H_3C–C(5)); 2.47–2.40 (m, 1H, H_2C(5')); 2.00–1.91 (m, 1H, H_2C(3')); 1.80–1.72 (m, 1H, H_2C(4')); 1.64–1.54 (m, 1H, H_2C(4')); 1.49–1.39 (m, 1H, H_2C(3')). ^{13}C NMR ($CDCl_3$): ´ 157.9 (C=O); 138.7, 137.5 (2 C(arom.)); 132.0, 131.7, 129.0, 128.8, 127.8, 122.2, 121.5, 116.7 (1 C(arom.), 9 CH(arom.), 2 C(imid.)); 126.1 (HC(2)); 62.8 (HC(2')); 60.3 (CH_2–Ph); 55.1 (C(5')); 48.8 (CH_2–N); 28.4 (C(3')); 23.7 (C(4')); 10.0 (H_3C–C(5)). HR-ESI-MS (MeOH + HCOOH): 469.1230 (calcd 469.1234 for $C_{23}H_{26}BrN_4O_2$, $[M(^{79}Br)+1]^+$). $[\pm]_D^{25}$ = –22 (*c* = 1.0, CH_2Cl_2).

4.2.5. Synthesis of imidazoles 6

To a magnetically stirred solution of an imidazole *N*-oxide **5** (5 mmol) in EtOH (15 ml), a suspension of freshly prepared Raney-Nickel in EtOH was added in small portions at rt. The progress of the reaction was followed by TLC (SiO_2, MeOH/AcOEt 1:1). Then, the mixture was filtered and the filtrate was concentrated under reduced pressure. The crude products **6a**-**e** were purified by chromatography or by crystallization.

4.2.5.1. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-4,5-dimethyl-1*H*-imidazole 6a

Yield: 1.0 g (75%). Pale yellow oil (SiO_2, MeOH/AcOEt, 1:1). IR (film): *v* 3428br, 2926m, 2854w, 2360w, 2342w, 1637w, 1560m, 1416m, 1245m, 1216m, 1045w, 1021w, 801m, 748m, 700m. ^{1}H NMR ($CDCl_3$): ´ 7.40 (s, 1H, HC(2)); 7.33–7.29 (m, 4H, HC(arom.)); 7.26–7.21 (m, 1H, HC(arom.)); 3.76 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 4.8, 1H, H_2C–N); 3.76, 3.44 (AB, J_{AB} = 13.2, 2H, H_2C–Ph); 3.66 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 7.2, 1H, H_2C–N); 3.31–2.96 (m, 1H, H_2C(5')); 2.87–2.82 (m, 1H, H_2C(2')); 2.33–2.27 (m, 1H, H_2C(5')); 2.13 (s, 3H, H_3C–C(4)); 2.06 (s, 3H, H_3C–C(5)); 1.89–1.81 (m, 1H, H_2C(3')); 1.73–1.65 (m, 2H, H_2C(4')); 1.57–1.49 (m, 1H, H_2C(3')). ^{13}C NMR ($CDCl_3$): ´ 139.2 (1 C(arom.)); 132.0 (HC(2)); 129.8, 129.0, 126.7, 121.1, 120.2 (5 CH(arom.); 2 C(imid.)); 63.5 (HC(2')); 59.1 (CH_2–Ph); 54.7 (C(5')); 49.6 (CH_2–N); 29.0 (C(3')); 23.3 (C(4')); 8.8 (H_3C–C(4)); 7.2 (H_3C–C(5)) ppm. HR-ESI-MS (MeOH + HCOOH): 270.1961 (calcd 270.1965 for $C_{17}H_{24}N_3$, $[M+1]^+$). $[\pm]_D^{25}$ = –25 (*c* = 1.0, CH_2Cl_2).

4.2.5.2. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-4-methyl-5-phenyl-1*H*-imidazole 6b

Yield: 1.2 g (70%). Pale yellow oil (SiO_2, MeOH/AcOEt, 1:1). IR (film): *v* 3583–3369br, 3059m, 3029m, 2948m, 2873m, 2796m, 1955m, 1888m, 1815m, 1688m, 1605w, 1493s, 1452m, 1207m, 1124m, 1029m, 966m, 701m. ^{1}H NMR ($CDCl_3$): ´ 7.58 (s, 1H, HC(2)); 7.46–7.41 (m, 2H, HC(arom.)); 7.39–7.35 (m, 1H, HC(arom.)); 7.30–7.26 (m, 4H, HC(arom.)); 7.24–7.20 (m, 1H, HC(arom.)); 7.19–7.17 (m, 2H, HC(arom.)); 3.92 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 4.8, 1H, H_2C–N); 3.76 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 7.2, 1H, H_2C–N); 3.55, 3.19 (AB, J_{AB} = 13.2, 2H, H_2C–Ph; 2.89–2.85 (m, 1H, H_2C(5')); 2.63–2.57 (m, 1H, HC(2')); 2.18 (s, 3H, H_3C–C(4)); 2.18–2.13 (m, 1H, H_2C(5')); 1.73–1.65 (m, 1H, H_2C(3')); 1.62–1.50 (m, 2H, H_2C(4')); 1.40–1.34 (m, 1H, H_2C(3')). ^{13}C NMR ($CDCl_3$): ´ 139.4, 135.6 (2 C(arom.)); 136.9 (HC(2)); 130.9, 130.5,

129.0, 128.9, 128.5, 128.1, 127.2 (7 signals for 10 HC(arom.) + 2 C(imid.)); 63.7 (C(2')); 59.5 (CH_2–Ph); 54.6 (C(5')); 49.8 (CH_2–N); 29.1 (C(3')); 23.1 (C(4')); 13.4 (H_3C–C(4)). HR-ESI-MS (MeOH + HCOOH): 332.2121 (calcd 332.2121 for $C_{22}H_{26}N_3$, $[M+1]^+$). $[\pm]_D^{25}$ = –25 (c = 1.0, CH_2Cl_2).

4.2.5.3. 4,5-Diphenyl-1-{[(2*S*)-*N*-benzylpyrrolidin-2-yl]methyl}-1*H*-imidazole 6c

Yield: 1.3 g (68%). Colorless crystals. Mp 118–119 °C (CH_2Cl_2/hexane). IR (KBr): ν 3432br, 3085m, 2971m, 2927m, 2905m, 2786m, 2723w, 1603m, 1505m, 1452m, 1369m, 1256m, 774m, 698s, 653m. ^{1}H NMR ($CDCl_3$): ´ 7.76 (s, 1H, HC(2)); 7.54–7.45 (m, 5H, HC(arom.)); 7.39–7.36 (m, 2H, HC(arom.)); 7.33–7.28 (m, 2H, HC(arom.)); 7.27–7.21 (m, 5H, HC(arom.)); 7.17–7.14 (m, 1H, HC(arom.)); 3.88 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 5.4, 1H, H_2C–N); 3.74 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 7.2, 1H, H_2C–N); 3.58, 3.25 (AB, J_{AB} = 12.6, 2H, H_2C–Ph); 2.96–2.91 (m, 1H, H_2C(5')); 2.72–2.66 (m, 1H, HC(2')); 2.26–2.19 (m, 1H, H_2C(5')); 1.83–1.76 (m, 1H, H_2C(4')); 1.70–1.58 (m, 2H, H_2C(3')); 1.52–1.45 (m, 1H, H_2C(4')). ^{13}C NMR ($CDCl_3$): ´ 139.2, 138.2, 134.9 (3 C(arom.)); 137.7 (HC(2)); 131.4, 131.3, 129.3, 129.0, 128.9, 128.7, 128.5, 128.3, 127.2, 126.8, 126.4 (15 CH(arom.), 2 C(imid.)); 63.7 (HC(2')); 59.6 (CH_2–Ph); 54.6 (H_2C(5')); 49.4 (CH_2–N); 29.1 (C(4')); 23.2 (C(3')). HR-ESI-MS (MeOH + HCOOH): 394.2278 (calcd 394.2278 for $C_{27}H_{28}N_3$, $[M+1]^+$). $[\pm]_D^{25}$ = –31 (c = 1.0, CH_2Cl_2).

4.2.5.4. *N*-Phenyl-1-{[(2*S*)-*N*-benzylpyrrolidin-2-yl]methyl}-5-methyl-1*H*-imidazole-4-carboxamide 6d

Yield: 1.3 g (72%). Colorless crystals. Mp 82–84 °C (Et_2O). IR (KBr): ν 3432br, 3270m, 3243m, 3121m, 3033m, 2969m, 2946m, 2779m, 1943w, 1968w, 1752w, 1660s, 1596s, 1537m, 1503s, 1440s, 1246s, 878m, 759s, 697s. ^{1}H NMR ($CDCl_3$): ´ 9.03 (s, 1H, NH); 7.70–7.67 (m, 2H, HC(arom.)); 7.48 (s, 1H, HC(2)); 7.35–7.28 (m, 6H, HC(arom.)); 7.27–7.24 (m, 1H, HC(arom.)); 7.09–7.07 (m, 1H, HC(arom.)); 3.81 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 4.8, 1H, H_2C–N); 3.76 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 6.0, 1H, H_2C–N); 3.75, 3.49 (AB, J_{AB} = 13.2, 2H, H_2C–Ph); 3.04–2.98 (m, 1H, H_2C(5')); 2.96–2.90 (m, 1H, HC(2')); 2.57 (s, 3H, H_3C–C(5)); 2.39–2.31 (m, 1H, H_2C(5')); 1.93–1.85 (m, 1H, H_2C(3')); 1.75–1.69 (m, 1H, H_2C(4')); 1.67–1.58 (m, 1H, H_2C(4')); 1.54–1.46 (m, 1H, H_2C(3')). ^{13}C NMR ($CDCl_3$): ´ 162.1 (C=O); 139.3, 138.7 (2 C(arom.)); 136.1 (HC(2)); 133.2, 131.5, 129.1, 128.9, 128.7, 127.5, 123.7, 119.7 (10 HC(arom.), 2 C(imid.)); 63.4 (HC(2')); 60.2 (CH_2–Ph); 55.0 (H_2C(5')); 49.0 (CH_2–N); 29.0 (C(3'));

23.4 (C(4')); 9.9 (H_3C–C(5)). HR-ESI-MS (MeOH + HCOOH): 375.2178 (calcd 375.2179 for $C_{23}H_{27}N_4O$, $[M+1]^+$). $[\pm]_D^{25} = -11$ (c = 1.0, CH_2Cl_2).

4.2.5.5. *N*-(4-Bromophenyl)-1-{[(2*S*)-*N*-benzylpyrrolidin-2-yl]methyl}-5-methyl-1*H*-imidazole-4-carboxamide 6e

Yield: 2.3 g (63%). Colorless oil (SiO_2, MeOH/AcOEt, 1:3). IR (film): ν 3362br, 3180s, 3061m, 3028m, 2970m, 2872m, 2799m, 1951m, 1888m, 1671m, 1588m, 1506m, 1397m, 1241m, 1116m, 1060m, 1007s, 829s, 700m, 659m. ^{1}H NMR ($CDCl_3$): ´ 9.03 (s, 1H, NH); 7.69–7.57 (m, 2H, HC(arom.)); 7.48 (s, 1H, HC(2)); 7.44–7.41 (m, 1H, HC(arom.)); 7.34–7.24 (m, 6H, HC(arom.)); 3.80–3.74 (m, 2H, H_2C–N); 3.73, 3.50 (AB, J_{AB} = 13.2, 2H, H_2C–Ph); 3.04–2.98 (m, 1H, H_2C(5')); 2.96–2.91 (m, 1H, HC(2')); 2.55 (s, 3H, H_3C–C(5)); 2.38–2.31 (m, 1H, H_2C(5')); 1.94–1.86 (m, 1H, H_2C(4')); 1.76–1.69 (m, 1H, H_2C(3')); 1.66–1.58 (m, 1H, H_2C(3')); 1.53–1.46 (m, 1H, H_2C(4')). ^{13}C NMR ($CDCl_3$): ´ 162.0 (C=O); 139.3, 137.8 (2 C(arom.)); 136.3 (HC(2)); 132.1, 129.1, 129.0, 128.7, 127.5, 121.2, 119.7, 116.1 (1 C(arom.), 9 CH(arom.), 2 C(imid.)); 63.4 (HC(2')); 60.2 (CH_2–Ph); 55.0 (H_2C(5')); 49.0 (CH_2–N); 29.0 (C(3')); 23.4 (C(4')); 9.9 (H_3C–C(5)). HR-ESI-MS (MeOH + HCOOH): 453.1279 (calcd 453.1285 for $C_{23}H_{26}BrN_4O$, $[M(^{79}Br)+1]^+$). $[\pm]_D^{25} = -10$ (c = 1.0, CH_2Cl_2).

4.2.6. General procedure for synthesis of imidazoles 7a and 7d

To a magnetically stirred solution of an imidazole *N*-oxide **5** (1 mmol) in MeOH (4 ml) 10% Pd/C (0.05 g) was added and the mixture stirred under H_2 atm until the reaction was completed (monitored by TLC). Then, the solid was filtered trough celite and the solvent was evaporated under reduced pressure. The obtained product was purified by column chromatography or by crystallization.

4.2.6.1. 4,5-Diphenyl-1-[(2*S*)-pyrrolidin-2-ylmethyl]-1*H*-imidazole 7a

Yield: 0.277 mg (87%). Colorless crystals. Mp 123–125 °C (CH_2Cl_2/hexane). IR (KBr): ν 3357br, 3049m, 2989m, 2834m, 2223w, 1509m, 1439m, 1357m, 1220m, 1033m, 907m, 895m, 802m, 731m. ^{1}H NMR ($CDCl_3$): ´ 7.74 (s, 1H, NH); 7.48–7.43 (m, 5H, HC(arom.)); 7.35–7.32 (m, 2H, HC(arom.)); 7.21–7.16 (m, 2H, HC(arom.)); 7.16–7.10 (m, 1H, HC(arom.)); 3.77 (dd, $^2J_{H,H}$ = 12.0, $^3J_{H,H}$ = 6.0, 1H, H_2C–N); 3.74 (dd, $^2J_{H,H}$ = 12.0, $^3J_{H,H}$ = 3.6, 1H, H_2C–N); 3.24–3.17 (m, 1H, HC(2')); 2.92–2.84 (m,

2H, $H_2C(5')$); 1.78–1.61 (m, 1H, $H_2C(3')$, 2H, $H_2C(4')$); 1.32–1.24 (m, 1H, $H_2C(3')$. ^{13}C NMR ($CDCl_3$): ´ 138.4, 137.4, 134.9, 131.3, 131.2, 129.3, 128.9, 128.6, 128.3, 126.8, 126.4 (10 HC(arom.), 2 (C(arom.), 3 C(imid.)); 58.6 (HC(2')); 50.5 (CH_2–N); 46.4 ($H_2C(5')$); 29.4 (C(4')); 25.3 (C(3')). HR-ESI-MS (MeOH + HCOOH): 302.1687 (calcd 302.1685 for $C_{17}H_{24}N_3S$, $[M+1]^+$). $[\pm]_D^{25} = -18$ (c = 1.0, CH_2Cl_2).

4.2.6.2. 5-Methyl-*N*-phenyl-1-[(2*S*)-pyrrolidin-2-ylmethyl]-1*H*-imidazole-4-carboxamide 7b

Yield: 0.235 mg (83%). Colorless oil (SiO_2, MeOH/AcOEt, 6:4). IR (film): v 3366br, 3058m, 2961m, 2873m, 2246w, 1663m, 1597m, 1575m, 1442m, 1330m, 1243m, 1064m, 906m, 877m, 829m, 756m. ^1H NMR ($CDCl_3$): ´ 9.05 (s, 1H, NH); 7.68–7.64 (m, 2H, HC(arom.)); 7.47 (s, 1H, HC(2)); 7.33–7.28 (m, 2H, HC(arom.)); 7.08–7.03 (m, 1H, HC(arom.)); 3.86 (dd, $^2J_{H,H}$ = 14.1, $^3J_{H,H}$ = 5.4, 1H, H_2C–N); 3.78 (dd, $^2J_{H,H}$ = 14.1, $^3J_{H,H}$ = 7.8, 1H, H_2C–N); 3.41–3.35 (m, 1H, HC(2')); 2.94–2.89 (m, 2H, $H_2C(5')$); 2.60 (s, 3H, H_3C–N); 1.93–1.86 (m, 1H, $H_2C(3')$); 1.84–1.68 (m, 2H, $H_2C(4')$); 1.44–1.37 (m, 1H, $H_2C(3')$). ^{13}C NMR ($CDCl_3$): ´ 162.1 (C=O); 138.6 (1 C(arom.)); 135.9, 133.1, 131.5, 129.0, 123.7, 119.7 (5 HC(arom.), 3 C(imid.)); 58.2 (CH_2–N); 50.1 (HC(2')); 46.5 ($H_2C(5')$); 29.4 (C(3')); 25.4 (C(4')); 9.8 (CH_3–N). HR-ESI-MS (MeOH + HCOOH): 302.1687 (calcd 302.1685 for $C_{17}H_{24}N_3S$, $[M+1]^+$). $[\pm]_D^{25} = -24$ (c = 1.0, CH_2Cl_2).

4.2.7. Synthesis of imidazole-2-thiones 9

To a magnetically stirred solution of an imidazole *N*-oxide **5** (4 mmol) in $CHCl_3$ (4 ml), 2,2,4,4-tetramethylcyclobutane-1,3-dithione **8** (2 mmol) in $CHCl_3$ (2ml) was added dropwise at 0 °C, and stirring was continued overnight at rt. Then, the solvent was evaporated under reduced pressure and the residue was washed with hexane. The resulting material was purified by crystallization.

4.2.7.1. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-4,5-dimethyl-1,3-dihydro-2*H*-imidazole-2-thione 9a

Yield: 0.8 g (68%). Colorless crystals. Mp 108–110 °C (CH_2Cl_2/hexane). IR (KBr): v 3432br, 3085m, 2943m, 2792m, 2522w, 1659s, 1499s, 1452m, 1393m, 1306m, 1127m, 1029m, 782m, 739s, 697s, 472s. ^1H NMR ($CDCl_3$): ´ 11.45 (s, 1H,

NH); 7.27–7.23 (m, 4H, HC(arom.)); 7.21–7.17 (m, 1H, HC(arom.)); 4.02 (dd, $^2J_{H,H}$ = 13.3, $^3J_{H,H}$ = 7.8, 1H, H_2C–N); 3.78 (dd, $^2J_{H,H}$ = 13.3, $^3J_{H,H}$ = 6.0, 1H, H_2C–N); 3.87, 3.45 (AB, J_{AB} = 13.2, 2H, H_2C–Ph); 3.41–3.34 (m, 1H, HC(2')); 2.99–2.94 (m, 1H, H_2C(5')); 2.28 (m, 1H, H_2C(5')); 2.03 (s, 3H, H_3C–C(4)); 2.01 (s, 3H, H_3C–C(5)); 1.88–1.63 (m, 2H, H_2C(4'), 2H, H_2C(3')). ^{13}C NMR ($CDCl_3$): ´ 158.5 (C=S); 139.2 (1 C(arom.)); 129.0, 128.3, 127.0, 122.2, 119.9 (5 HC(arom.), 1 (C(arom.), 2 C(imid.)); 61.9 (HC(2')); 60.5 (CH_2–Ph); 54.8 (H_2C(5')); 49.4 (CH_2–N); 29.2 (C(4')); 23.6 (C(3')); 9.3 (H_3C–C(5)); 9.2 (H_3C–C(4)). HR-ESI-MS (MeOH + HCOOH): 302.1687 (calcd 302.1685 for $C_{17}H_{24}N_3S$, $[M+1]^+$). $[\pm]_D^{25}$ = –19 (c = 1.0, CH_2Cl_2).

4.2.7.2. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-4,5-diphenyl-1,3-dihydro-2*H*-imidazole-2-thione 9b

Yield: 0.5 g (31%). Colorless crystals. Mp 197–199 °C (EtOH). IR (KBr): *v* 3432br, 3058m, 2937m, 2807m, 1602m, 1492s, 1397s, 1202m, 1160m, 1119m, 1073m, 1027m, 700s, 682m, 556s. ^{1}H NMR ($CDCl_3$): ´ 11.30 (s, 1H, NH); 7.46–7.40 (m, 3H, HC(arom.)); 7.36–7.33 (m, 2H, HC(arom.)); 7.25–7.16 (m, 10H, HC(arom.)); 4.12 (dd, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 9.0, 1H, H_2C–N); 3.94 (dd, $^2J_{H,H}$ = 12.9, $^3J_{H,H}$ = 4.2, 1H, H_2C–N); 3.76, 3.22 (AB, J_{AB} = 12.9, 2H, H_2C–Ph); 3.21–3.25 (m, 1H, HC(2')); 2.81–2.76 (m, 1H, H_2C(5')); 2.20–2.15 (m, 1H, H_2C(5')); 1.73–1.66 (m, 1H, H_2C(4')). ^{13}C NMR ($CDCl_3$): ´ 161.4 (C=S); 140.1 (1 C(arom.)); 131.7, 129.6, 129.3, 129.1, 129.0, 128.9, 128.3, 128.1, 127.9, 126.9, 126.8, 125.5 (12 signals for 15 HC(arom.), 3 C(arom.), 2 C(imid.)); 61.7 (HC(2')); 59.9 (CH_2–Ph); 54.3 (C(5')); 49.3 (CH_2–N); 29.1 (C(3')); 23.5 (C(4')). HR-ESI-MS (MeOH + HCOOH): 426.1998 (calcd 426.1999 for $C_{27}H_{28}N_3S$, $[M+1]^+$). $[\pm]_D^{25}$ = –14 (c = 1.0, CH_2Cl_2).

4.2.7.3. *N*-(4-Bromophenyl)-1-{[(2*S*)-*N*-benzylpyrrolidin-2-yl]methyl}-5-methyl-2-thioxo-2,3-dihydro-1*H*-imidazole-4-carboxamide 9c

Yield: 0.8 g (41%). Colorless crystals. Mp 215 °C (EtOH) (decomposition). IR (KBr): *v* 3432br, 3275m, 3125m, 3065m, 2952m, 2902w, 2787m, 1663s, 1625s, 1542s, 1489s, 1380m, 828m, 811m, 698m, 504m. ^{1}H NMR ($CDCl_3$): ´ 8.85 (s, 1H, HN); 7.73–7.66 (m, 2H, HC(arom.)); 7.45–7.41 (m, 2H, HC(arom.)); 7.24–7.20 (m, 4H, HC(arom.)); 7.15–7.10 (m, 1H, HC(arom.)); 4.11 (dd, $J_{H,H}$ = 13.3, $J_{H,H}$ = 5.8, 1H, H_2C–N); 3.85 (dd, $J_{H,H}$ = 13.3, $J_{H,H}$ = 6.0, 1H, H_2C–N); 3.74, 3.19 (AB, J_{AB} = 12.9, 2 H, H_2C–Ph); 3.42–3.33 (m, 1H, H_2C(5')); 3.08–3.02 (m, 1H, HC(2')); 2.57 (s, 3H, H_3C–

C(5)); 2.46–2.35 (m, 1H, $H_2C(5')$); 1.92–1.85 (m, 1H, $H_2C(4')$); 1.83–1.68 (m, 2H, $H_2C(3')$, 1H $H_2C(4')$). ^{13}C NMR ($CDCl_3$): ´ 162.1 (C=S); 161.6 (C=O); 138.7, 138.0 (2 C(arom.)); 136.6 (HC(2)); 132.7, 129.6, 129.1, 128.9, 121.7, 119.7, 116.1 (9 HC(arom.), 1 C(arom.)), 2 C(imid.)); 63.8 (C(2')); 60.9 (CH_2–Ph); 55.3 (C(5')); 49.2 (CH_2–N); 29.7 (C(3')); 23.1 (C(4')); 10.0 (H_3C–C(5)). HR-ESI-MS (MeOH + HCOOH): 485.1002 (calcd 485.1005 for $C_{23}H_{26}BrN_4OS$, $[M+1]^+$). $[\pm]_D^{25}$ = –10 (c = 1.0, CH_2Cl_2).

4.2.8. Synthesis of 3-alkylimidazolium tetrafluoroborates 11

A solution of an imidazole **6** (5 mmol) and an alkyl bromide (5 mmol) in acetonitrile (5 ml) was heated at reflux for 16 h. Then, the solvent was removed under reduced pressure, the resulting product was washed with Et_2O (3×5 ml), and dried under high vacuum for 4 h. The imidazolium bromide obtained was magnetically stirred with an equimolar amount of solid $NaBF_4$ in acetone (5 ml) overnight at rt. The resulting suspension was filtered through neutral alumina ($CHCl_3$) and the solvent evaporated under reduced pressure.

4.2.8.1. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-3-hexyl-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate 11a

Yield: 1.6 g (75%). Pale yellow oil (Al_2O_3, $CHCl_3$). IR (film): *v* 3648w, 3628w, 3566m, 3154m, 3087m, 2956m, 2931m, 2805m, 1818m, 1564m, 1455m, 1058br, 742m, 703m, 626m. ^1H NMR ($CDCl_3$): ´ 8.72 (HC(2)); 7.29–7.26 (m, 2H, HC(arom.)); 7.23–7.19 (m, 3H, HC(arom.)); 4.01–3.95 (m, 1H, H_2C–N, 2H, H_2C(alk.)); 3.89 (dd, $^2J_{H,H}$ = 13.8, $^3J_{H,H}$ = 6.6, 1H, H_2C–N); 3.59, 3.56 (AB, J_{AB} = 13.2, 2H, H_2C–Ph); 3.16–3.11 (m, 1H, HC(2')); 3.10–3.06 (m, 1H, $H_2C(5')$); 2.50–2.45 (m, 1H, $H_2C(5')$); 2.16 (s, 3H, H_3C–C(4)); 2.12 (s, 3H, H_3C–C(5)); 2.05–1.98 (m, 1H, $H_2C(3')$); 1.83–1.77 (m, 1H, $H_2C(4')$); 1.74–1.67 (m, 1H, $H_2C(4')$; 2H, H_2C(alk.)); 1.55–1.50 (m, 1H, $H_2C(3')$); 1.32–1.24 (m, 6H, H_2C(alk.)); 0.85 (t, $J_{H,H}$ = 7.2, 3H, H_3C(alk.)). ^{13}C NMR ($CDCl_3$): ´ 139.4 (1 C(arom.); 135.4 (HC(2)); 128.9, 128.5, 127.3, 127.2, 126.0 (5 CH(arom.), 2 C(imid.)); 62.7 (HC(2')); 60.5 (CH_2–Ph); 54.9 ($H_2C(5')$); 50.8 (CH_2–N); 47.4, 31.3, 29.9 (3 C(alk.)); 28.5 (C(4')); 26.1 (C(alk.)); 23.9 (C(3')); 22.6 (C(alk.)); 14.1 (H_3C(alk.)); 8.7 (H_3C–C(5)); 8.5 (H_3C–C(4)). $[\pm]_D^{25}$ = –35 (*c* = 1.0, CH_2Cl_2).

4.2.8.2. 1-{[(2*S*)-*N*-Benzylopyrrolidin-2-yl]methyl}-4,5-dimethyl-3-octyl-1*H*-imidazolium tetrafluoroborate 11b

Yield: 1.6 g (70%). Pale yellow oil (Al_2O_3, $CHCl_3$). IR (film): *v* 3584w, 3154m, 3087m, 2928m, 2857m, 2806m, 1733w, 1699w, 1565s, 1454m, 1202m, 1058br, 828w, 742m, 703m. ^{1}H NMR ($CDCl_3$): ´ 8.73 (s, 1H, HC(2)); 7.28–7.25 (m, 2H, HC(arom.)); 7.23–7.18 (m, 3H, HC(arom.)); 3.98 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 5.4, 1H, H_2C–N); 3.97–3.94 (m, 2H, H_2C(alk.)); 3.88 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 7.2, 1H, H_2C–N); 3.57, 3.55 (AB, J_{AB} = 13.6, 2H, H_2C–Ph); 3.16–3.11 (m, 1H, H_2C(2')); 3.10–3.05 (m, 1H, H_2C(5')); 2.50–2.44 (m, 1H, H_2C(5')); 2.15 (s, 3H, H_3C–C(4)); 2.10 (s, 3H, H_3C–C(5)); 1.97–1.82 (m, 1H, H_2C(3')); 1.82–1.77 (m, 1H, H_2C(3')); 1.74–1.67 (m, 1H, H_2C(4'), 2H, H_2C(alk.)); 1.55–1.49 (m, 1H, H_2C(4')); 1.31–1.21 (m, 10H, H_2C(alk.)); 8.62 (t, $J_{H,H}$ = 6.9, H_3C(alk.)). ^{13}C NMR ($CDCl_3$): ´ 139.3 (1 C(arom.); 135.4 (HC(2)); 128.9, 128.5, 127.2, 127.2, 126.0 (5 HC(arom.), 2 C(imid.)); 62.6 (HC(2')); 60.4 (CH_2–Ph); 54.9 (C(5')); 50.8 (CH_2–N); 47.4, 31.8, 29.9, 29.2, 29.1 (5 C(alk.)); 28.4 (C(3')); 26.5 (C(alk.)); 23.9 (C(4')); 22.7 (C(alk.)); 14.2 (H_3C(alk.)); 8.7 (H_3C–C(4)); 8.5 (H_3C–C(5)). $[\pm]_D^{25}$ = –22 (*c* = 1.0, CH_2Cl_2).

4.2.8.3. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-3-butyl-4-methyl-5-phenyl-1*H*-imidazolium tetrafluoroborate 11c

Yield: 1.6 g (68%). Pale yellow oil (Al_2O_3, $CHCl_3$). IR (film): *v* 3151m, 3084m, 2961m, 2874m, 2807m, 1559m, 1497m, 1453m, 1203m, 1058m, 846w, 765m, 703s. ^{1}H NMR ($CDCl_3$): ´ 8.91 (s, 1H, HC(2)); 7.55–7.50 (m, 3H, HC(arom.)); 7.29–7.26 (m, 4H, HC(arom.)); 7.24–7.21 (m, 1H, HC(arom.)); 7.17–7.15 (m, 2H, HC(arom.)); 4.09–4.07 (m, 2H, H_2C(alk.)); 3.97 (dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 5.4, 1H, H_2C–N); 3.93 (dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 6.6, 1H, H_2C–N); 3.52, 3.43 (AB, J_{AB} = 13.2, 2H, H_2C–Ph); 3.00–2.96 (m, 1H, H_2C(5')); 2.93–2.88 (m, 1H, H_2C(2')); 2.43–2.37 (m, 1H, H_2C(5')); 2.16 (s, 3H, H_3C–C(4)); 1.86–1.76 (m, 1H, H_2C(3'), 2H, H_2C(alk.)); 1.74–1.66 (m, 1H, H_2C(4')); 1.60–1.53 (m, 1H, H_2C(4')); 1.44–1.38 (m, 2H, H_2C(alk.)); 1.36–1.31 (m, 1H, H_2C(3')); 0.97 (t, $J_{H,H}$ = 7.50 Hz, H_3C(alk.)). ^{13}C NMR ($CDCl_3$): ´ 139.3 (1 C(arom.)); 136.2 (HC(2)), 131.7, 130.9, 130.7, 129.7, 128.9, 128.5, 127.5, 127.3, 125.6 (10 HC(arom.), 1 C(arom.), 2 C(imid.)); 62.6 (HC(2')); 59.9 (CH_2–Ph); 54.4 (H_2C(5')); 50.9 (CH_2–N); 47.6, 31.8 (2 C(alk.)); 28.4 (C(3')); 23.7 (C(4')); 19.8 (C(alk.)); 13.6 (H_3C(alk.)); 8.9 (H_3C–C(4)). $[\pm]_D^{25}$ = –10 (*c* = 1.0, CH_2Cl_2).

4.2.8.4. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-4-methyl-3-octyl-5-phenyl-1*H*-imidazolium tetrafluoroborate 11d

Yield: 1.9 g (72%). Pale yellow oil (Al_2O_3, $CHCl_3$). IR (film): *v* 3627w, 3557w, 3151m, 3062m, 2927m, 2857m, 2804m, 1966m, 1900m, 1822m, 1559m, 1496m, 1459m, 1208m, 1058m, 926m, 843m, 763s, 703m. ^{1}H NMR ($CDCl_3$): ´ 9.00 (s, 1H, HC(2)); 7.55–7.50 (m, 3H, HC(arom.)); 7.29–7.26 (m, 4H, HC(arom.)); 7.24–7.21 (m, 1H, HC(arom.)); 7.18–7.16 (m, 2H, HC(arom.)); 3.99 (dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 5.4, 1H, H_2C–N); 3.94 (dd, $^2J_{H,H}$ = 14.0, $^3J_{H,H}$ = 6.6, 1H, H_2C–N); 3.54, 3.43 (AB, J_{AB} = 13.2, 2H, H_2C–Ph); 3.00–2.96 (m, 1H, H_2C(5')); 2.94–2.90 (m, 1H, HC(2')); 2.42–2.37 (m, 1H, H_2C(5')); 2.16 (s, 3H, H_3C–C(5)); 1.87–1.77 (m, 2H, H_2C(alk.), 1H, H_2C(4')); 1.73–1.67 (m, 1H, H_2C(3')); 1.60–1.52 (m, 1H, H_2C(3')); 1.39–1.21 (m, 10H, H_2C(alk.), 1H, H_2C(4')); 0.87 (t, $J_{H,H}$ = 7.2, H_3C(alk.)). ^{13}C NMR ($CDCl_3$): ´ 139.3 (1 C(arom.); 136.2 (HC(2)); 131.7, 130.8, 130.7, 129.6, 128.9, 128.5, 127.5, 127.2, 125.5 (10 HC(arom.), 2 C(arom.) 2 C(imid.)); 62.6 (C(2')); 59.9 (CH_2–Ph); 54.4 (H_2C(5')); 50.8 (CH_2-N); 47.8, 31.9, 29.9, 29.2 (4 C(alk.)); 29.2 (C(3')); 28.3, 26.6 (2 C(alk.)); 23.7 (C(4')); 22.8 (C(alk.)); 14.2 (H_3C(alk.)); 8.9 (H_3C–C(5)). $[\pm]_D^{25}$ = –27 (*c* = 1.0, CH_2Cl_2).

4.2.9. Synthesis of 3-alkoxyimidazolium tetrafluoroborates 13

A solution of an imidazole *N*-oxide **5** (5 mmol) and the corresponding alkyl bromide (5 mmol) in $CHCl_3$ (10 ml) was magnetically stirred at rt for 72 h. Then, the solvent was removed under reduced pressure and the crude product was washed with Et_2O (3×5 ml), and dried under high vacuum for 4 h. The imidazolium bromide obtained was magnetically stirred with an equimolar amount of solid $NaBF_4$ in acetone (5 ml) at rt overnight. The resulting suspension was filtered through neutral alumina (Et_2O) and the solvent evaporated under reduced pressure.

4.2.9.1. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-3-butoxy-4,5-dimethyl-1*H*-imidazolium tetrafluoroborate 13a

Yield: 1.8 g (78%). Pale yellow oil (Al_2O_3, $CHCl_3$). IR (film): *v* 3585w, 3380m, 3140m, 2961m, 2874m, 2807m, 1684m, 1545m, 1496m, 1454m, 1259w, 1187w, 1058m, 936m, 848m, 820m, 735s, 703s, 613w. ^{1}H NMR ($CDCl_3$): ´ 9.28 (s, 1H, HC(2)); 7.31–7.14 (m, 5H, HC(arom.)); 4.38–4.29 (m, 2H, H_2C(alk.)); 4.09 (dd, $^2J_{H,H}$ =

14.4, $^{3}J_{H,H}$ = 4.8, 1H, H_2C–N); 3.96 (dd, $^{2}J_{H,H}$ = 14.4, $^{3}J_{H,H}$ = 7.8, 1H, H_2C–N); 3.59, 3.56 (AB, J_{AB} = 13.2, 1H, H_2C–Ph); 3.19–3.11 (m, 1H, H_2C(5'), 1H, HC(2')); 2.57–2.52 (m, 1H, H_2C(5')); 2.15 (s, 3H, H_3C–C(4)); 2.08 (s, 3H, H_3C–C(5)); 2.06–2.00 (m, 1H, H_2C(3')); 1.86–1.79 (m, 1H, H_2C(4')); 1.79–1.71 (m, 2H, H_2C(alk.), 1H, H_2C(4')); 1.56–1.44 (m, 2H, H_2C(alk.); 1H, H_2C(3')); 0.97 (t, $J_{H,H}$ = 7.2, H_3C(alk.)). ^{13}C NMR ($CDCl_3$): ´ 139.2 (1 C(arom.)); 131.7 (HC(2)); 129.0, 128.5, 127.3, 124.8, 123.5 (5 CH(arom.), 2 C(imid.)); 82.9 (C(alk.)); 62.5 (C(2')); 60.6 (CH_2–Ph); 55.0 (C(5')); 50.9 (CH_2–N); 29.9 (C(alk.)); 28.3 (C(3')); 24.0 (C(4')); 19.0 (C(alk.)); 13.9 (H_3C(alk.)); 8.7 (H_3C-C(5)); 7.2 (H_3C–C(4)). $[\pm]_D^{25}$ = –33 (c = 1.0, CH_2Cl_2).

4.2.9.2. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-4,5-dimethyl-3-octyloxy-1*H*-imidazolium tetrafluoroborate 13b

Yield: 1.7 g (69%). Pale yellow oil (Al_2O_3, $CHCl_3$). IR (film): *v* 3584w, 3566w, 3384m, 3139m, 3061m, 2928m, 2857m, 2807m, 1634m, 1546m, 1496w, 1454w, 1260w, 1059m, 945m, 807w, 736m, 703s, 648w. ^{1}H NMR ($CDCl_3$): ´ 8.91 (s, 1H, HC(2)); 7.27–7.19 (m, 3H, HC(arom.)); 7.17–7.13 (m, 2H, HC(arom.)); 4.36–4.27 (m, 2H, H_2C(alk.)); 4.05 (dd, $^{2}J_{H,H}$ = 14.4, $^{3}J_{H,H}$ = 4.8, 1H, H_2C–N); 3.93 (dd, $^{2}J_{H,H}$ = 14.4, $^{3}J_{H,H}$ = 7.8, 1H, H_2C–N); 3.57, 3.55 (AB, J_{AB} = 13.2, 2H, H_2C–Ph); 3.16–3.10 (m, 1H, H_2C(5'), 1H, HC(2')); 2.57–2.52 (m, 1H, H_2C(5')); 2.15 (s, 3H, H_3C–C(4)); 2.08 (s, 3H, H_3C–C(5)); 2.07–2.01 (m, 1H, H_2C(3')); 1.86–1.80 (m, 1H, H_2C(4')); 1.78–1.71 (m, 2H, H_2C(alk.); 1H, H_2C(4')); 1.54–1.49 (m, 1H, H_2C(3')); 1.56–1.40 (m, 2H, H_2C(alk.)); 1.35–1.24 (m, 8H, H_2C(alk.)); 0.89 (t, $J_{H,H}$ = 7.2, 3H, H_3C(alk.)). ^{13}C NMR ($CDCl_3$): ´ 139.4 (1 C(arom.)); 131.3 (HC(2)); 129.0, 128.5, 127.3, 124.8, 123.5 (5 C(arom.), 2 C(imid.)); 62.4 (HC(2')); 60.6 (CH_2–Ph); 54.9 (C(5')); 50.9 (CH_2–N); 29.4, 28.3 (2 C(alk.)); 28.0 (C(3')); 25.7 (C(alk.)); 24.0 (C(4')); 22.8 (C(alk.)); 14.3 (H_3C(alk.)); 8.7 (H_3C–C(5)), 7.3 (H_3C–C(4)). $[\pm]_D^{25}$ = –26 (c = 1.0, CH_2Cl_2).

4.2.9.3. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-3-butoxy-4-methyl-5-phenyl-1*H*-imidazolium tetrafluoroborate 13c

Yield: 1.6 g (70%). Pale yellow oil (Al_2O_3, $CHCl_3$). IR (film): *v* 3584w, 3366m, 3135m, 3061m, 2961m, 2874m, 2806m, 1679m, 1543m, 1496m, 1452m, 1380m, 1283w, 1058m, 934m, 822w, 756m, 736m, 702s. ^{1}H NMR ($CDCl_3$): ´ 9.08 (s, 1H, HC(2)); 7.53–7.48 (m, 3H, HC(arom.)); 7.28–7.13 (m, 7H, HC(arom.)); 4.52–4.43 (m, 2H, H_2C(alk.)); 4.04 (dd, $^{2}J_{H,H}$ = 14.4, $^{3}J_{H,H}$ = 4.8, 1H, H_2C–N); 3.95 (dd, $^{2}J_{H,H}$ = 14.4,

$^{3}J_{H,H}$ = 7.8, 1H, H_2C–N); 3.57, 3.45 (AB, J_{AB} = 12.6, 2H, H_2C–Ph); 3.06–3.02 (m, 1H, $H_2C(5')$); 2.91–2.86 (m, 1H, HC(2')); 2.52–2.47 (m, 1H, $H_2C(5')$); 2.16 (s, 3H, H_3C–C(4)); 1.86–1.79 (m, 2H, H_2C(alk.), 1H, $H_2C(3')$); 1.78–1.71 (m, 1H, $H_2C(4')$); 1.63–1.50 (m, 2H, H_2C(alk.); 1H, $H_2C(4')$); 1.43–1.28 (m, 1H, $H_2C(3')$); 1.00 (t, $J_{H,H}$ = 7.2, 3H, H_3C(alk.)). ^{13}C NMR ($CDCl_3$): ´ 139.3 (1 C(arom.)); 132.1 (HC(2)); 130.9, 130.8, 129.7, 129.1, 129.0, 128.5, 127.3, 124.9, 124.8 (10 HC(arom.); 1 C(arom.), 2 C(imid.)); 83.2 (C(alk.)); 62.3 (HC(2')); 60.1 (CH_2–Ph); 54.4 (C(5')); 50.6 (CH_2–N); 30.1 (C(alk.)); 27.9 (C(4')); 23.8 (C(3')); 19.1, 13.9 (2 C(alk.)); 7.5 (H_3C–C(4)). $[\pm]_D^{25}$ = –25 (c = 1.0, CH_2Cl_2).

4.2.9.4. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-3-hexyloxy-4-methyl-5-phenyl-1*H*-imidazolium tetrafluoroborane 13d

Yield: 1.9 g (76%). Pale yellow oil (Al_2O_3, $CHCl_3$). IR (film): *v* 3584w, 3369m, 3135m, 3061m, 2930m, 2872m, 2807m, 1683m, 1542m, 1496m, 1453m, 1379m, 1283w, 1058m, 933m, 913m, 765m, 735m, 702s. ^{1}H NMR ($CDCl_3$): ´ 9.10 (s, 1H, HC(2)); 7.55–7.48 (m, 3H, HC(arom.)); 7.29–7.14 (m, 7H, HC(arom.)); 4.51–4.42 (m, 2H, H_2C(alk.)); 4.04 (dd, $^{2}J_{H,H}$ = 14.0, $^{3}J_{H,H}$ = 4.8, 1H, H_2C–N); 3.95 (dd, $^{2}J_{H,H}$ = 14.0, $^{3}J_{H,H}$ = 7.8, 1H, H_2C–N); 3.57, 3.45 (AB, J_{AB} = 13.2, 2H, H_2C–Ph); 3.06–3.02 (m, 1H, $H_2C(5')$); 2.92–2.87 (m, 1H, HC(2')); 2.53–2.47 (m, 1H, $H_2C(5')$); 2.16 (s, 3H, H_3C–C(4)); 1.87–1.80 (m, 2H, H_2C(alk.); 1H, $H_2C(3')$); 1.78–1.71 (m, 1H, $H_2C(4')$); 1.64–1.57 (m, 1H, $H_2C(4')$); 1.51–1.46 (m, 2H, H_2C(alk.)); 1.37–1.28 (m, 4H, H_2C(alk.), 1H, $H_2C(3')$); 0.92 (t, $J_{H,H}$ = 6.9, 3H, H_3C(alk.)). ^{13}C NMR ($CDCl_3$): ´ 139.3 (1 C(arom.)); 132.1 (HC(2)); 131.0, 130.9, 129.6, 129.1, 129.0, 128.5, 127.3, 124.9, 124.8 (10 HC(arom.); 1 C(arom.), 2 C(imid.)); 83.5 (C(alk.)); 62.3 (HC(2')); 60.1 (CH_2–Ph); 54.4 (C(5')); 50.6 (CH_2–N); 31.6, 28.1 (2 C(alk.)); 27.9 (C(3')); 25.4 (C(alk.)); 23.8 (C(4')); 22.7 (C(alk.)); 14.2 (H_3C(alk.)); 7.6 (H_3C–C(4)). $[\pm]_D^{25}$ = –17 (c = 1.0, CH_2Cl_2).

4.2.9.5. 1-{[(2*S*)-*N*-Benzylpyrrolidin-2-yl]methyl}-3-butoxy-4,5-diphenyl-1*H*-imidazolium tetrafluoroborate 13e

Yield: 1.5 g (53%). Pale yellow oil (Al_2O_3, $CHCl_3$). IR (film): *v* 3648w, 3584w, 3369w, 3135m, 3061m, 2961m, 2874m, 2808m, 1683m, 1494m, 1447m, 1271m, 1179m, 1058m, 934m, 819m, 763m, 735m, 700m, 607w. ^{1}H NMR ($CDCl_3$): ´ 9.24 (s, 1H, HC(2)); 7.50–7.20 (m, 15H, HC(arom.)); 4.26–4.19 (m, 1H, H_2C–N, 2H, H_2C(alk.)); 4.10 (dd, $^{2}J_{H,H}$ = 13.8, $^{3}J_{H,H}$ = 7.2, 1H, H_2C–N); 3.65, 3.49 (AB, J_{AB} = 13.2,

2H, H_2C–Ph); 3.06–3.01 (m, 1H, $H_2C(5')$); 2.98–2.92 (m, 1H, HC(2')); 2.53–2.47 (m, 1H, $H_2C(5')$); 1.89–1.82 (m, 1H, $H_2C(3')$); 1.79–1.73 (m, 1H, $H_2C(4')$); 1.64–1.56 (m, 2H, H_2C(alk.); 1H, $H_2C(4')$); 1.36–1.32 (m, 1H, $H_2C(3')$); 1.31–1.24 (m, 2H, H_2C(alk.)); 0.79 (t, $J_{H,H}$ = 7.5, 3H, H_3C(alk.)). ^{13}C NMR ($CDCl_3$): ´ 139.3 (1 C(arom.)); 133.1 (HC(2)); 131.3, 130.9, 130.4, 129.8, 129.73, 129.68, 129.2, 129.1, 128.7, 127.6, 126.8, 124.6, 123.4 (15 HC(arom.), 2 C(arom.) 2 C(imid.)); 83.4 (C(alk.)); 62.3 (C(2')); 59.8 (CH_2–Ph); 54.1 (C(5')); 50.4 (CH_2–N); 29.8 (C(alk.)); 23.6 (C(3')); 18.8 (C(4')); 13.7 (H_3C(alk.)). $[\pm]_D^{25}$ = –16 (c = 1.0, CH_2Cl_2).

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